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(54) Rubber composition

Kautschukmischung

Composition de caoutchouc

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(56) References cited:

GB-A- 909 753 GB-A- 1 330 393 US-A- 4 124 750 US-A- 4 607 060

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## Description

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The present invention relates to a rubber composition having improved low heat generation properties, for use in a pneumatic tire.

In response to social demands of resource saving and energy saving, the development of tires having low fuel consumption has been vigorously carried out for several years in the rubber industry, in particular in the tire industry.

For the development of low fuel consumption tires, low heat generating rubber compositions are indispensable.

Japanese Patent Application Laid-open No. 23409/1985 discloses that styrene-butadiene rubber (SBR), the ends of one molecule of which are modified with a particular compound, may be used for lowering the heat generation, in particular in the field of tires of passenger cars. This method can be applied to a solution-polymerized SBR, but cannot be effectively applied to other rubbers, in particular natural rubber which is widely used for tires of heavy vehicles and emulsion-polymerized SBR having excellent high temperature breaking characteristics.

Attention is also drawn to the disclosures of GB-A-909753, US-A-4124750, US-A-4607060, and GB-A-1330393. An object of the present invention is to provide a rubber composition having improved heat generation characteristics, for use in pneumatic tires.

According to the present invention, there is provided the use of a rubber composition having improved low heat generation properties in a pneumatic tire, comprising:

100 parts by weight of at least one rubber selected from natural rubber, synthetic polyisoprene rubber, styrenebutadiene rubber and polybutadiene rubber;

20 to 150 parts by weight of a reinforcing filler; and

0.05 to 20 parts by weight of a compound selected from isophthalic dihydrazide and 2-hydroxy-3-naphthoic hydrazide.

The compounds isophthalic dihydrazide and 2-hydroxy-3-naphthoic hydrazide exhibit excellent heat generation improving effect when they are compounded in rubber. The compound is preferably 2-hydroxy-3-naphthoic hydrazide.

Rubbers which may be used in the present invention are natural rubber, synthetic polyisoprene rubber, styrene-butadiene copolymer rubber, and polybutadiene rubber. These rubbers may be used alone or in combination. The rubber is preferably natural rubber or synthetic polyisoprene rubber.

In the present invention, the above-mentioned heat generation improvers may be used alone or in combination. The amount of the heat generation improver to be compounded is 0.05 - 20 parts by weight, preferably 0.1 - 5 parts, and more preferably 0.25 - 5 parts.

When the amount of the heat generation improver is less than 0.05 part by weight, the heat generation improving effect can be hardly expected. When the amount exceeds 20 parts by weight, the heat generation improving effect does not increase any more and sometimes mechanical properties of the rubber composition decrease.

As the reinforcing filler used in the present invention, there may be mentioned carbon black and the like, and the amount to be used is 20 - 150 parts by weight.

When the amount of reinforcing filler is less than 20 parts by weight, the rubber composition is not sufficiently reinforced. When the amount exceeds 150 parts by weight, the heat generation characteristics of rubber become worse and in addition the abrasion resistance and other physical properties are deteriorated.

In the present invention, if necessary, there may be appropriately added to the rubber composition softening agents, antioxidants, vulcanization accelerators, vulcanization accelerating auxiliary agents, vulcanizing agents and the like which are additives usually used in the rubber industry.

The invention will be further described with reference to the following illustrative examples.

### Examples 1 and 2 and Comparison Example 1

One hundred parts by weight of natural rubber was compounded with 50 parts by weight of ISAF carbon black, 3 parts by weight of stearic acid, one part by weight of N-(1,3-dimethylbutyl)-N<sup>1</sup>-phenyl-p-phenylenediamine, 5 parts by weight of zinc oxide, one part by weight of N-tert-butyl-2-benzothiazole sulfeneamide, 1.5 parts by weight of sulfur and 1/200 mole of a heat generation improver selected from Table 1 to prepare a rubber composition.

In the same manner, various rubber compositions were prepared using the heat generation improvers in Table 1. The resulting rubber compositions were kneaded with a Banbury mixer and vulcanized to prepare samples. The low heat generation characteristic was evaluated.

For comparison, a sample prepared by repeating the above-mentioned procedure except that no heat generation improver was added was also evaluated as to the low heat generation characteristic.

The results are shown in Table 1. The low heat generation index was calculated by the following formula where  $\tan \delta$  was measured at 50°C at a dynamic strain of 5% with a frequency of 15 Hz by means of a viscoelasticity measuring

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apparatus manufactured by Rheometric Co.

Low heat generation index =  $\frac{\tan \delta \text{ (Blank)}}{\tan \delta \text{ (Heat generation improver compounded rubber)}} X 100$ 

The larger this index, the less the heat generation.

Table 1

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Heat generation Compounded Low heat improver amount generation index

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Example Isophthalic 0.97 156 dihydrazide

0 C-NHNH<sub>2</sub> C-NHNH<sub>2</sub>

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Example 2-Hydroxy-3-naphthoic 1.01 154 2 hydrazide

OTOTOH C-NH-NH<sub>2</sub>

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Comparison (Blank) \_\_\_\_ 100
Example

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As is clear from the Examples, the rubber heat generation improvers of the present invention exhibit a remarkable heat generation improving effect even when they are incorporated in rubber components such as natural rubber.

Therefore, the rubber composition of the present invention containing a specified amount of the heat generation improver and of a reinforcing filler exhibits a significantly lowered heat generation without previously modifying the structure of rubber as compared with rubber compositions containing no heat generation improver.

#### Claims

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- 10 1. The use of a rubber composition having improved low heat generation properties in a pneumatic tire, comprising:
  - 100 parts by weight of at least one rubber selected from natural rubber, synthetic polyisoprene rubber, styrenebutadiene rubber and polybutadiene rubber;
  - 20 to 150 parts by weight of a reinforcing filler: and
  - 0.05 to 20 parts by weight of a compound selected from isophthalic dihydrazide and 2-hydroxy-3-naphthoic hydrazide.
  - 2. The use of a rubber composition as claimed in claim 1, characterized in that said compound is 2-hydroxy-3-naphthoic hydrazide.
  - 3. The use of a rubber composition as claimed in claim 1 or 2, characterized in that said rubber is natural rubber or synthetic polyisoprene rubber.
- 4. The use of a rubber composition as claimed in any of claims 1 to 3, characterized in that said compound is present 25 in an amount of 0.1 to 5 parts by weight.
  - 5. The use of a rubber composition as claimed in claim 4. characterized in that said compound is present in an amount of 0.25 to 5 parts by weight.
- 30 6. The use of a rubber composition as claimed in any of claims 1 to 5, characterized in that said reinforcing filler is carbon black.

### Patentansprüche

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  - 1. Verwendung einer Kautschukzusammensetzung mit verbesserten Wärmeentwicklungseigenschaften in einem Luftreifen, welche aufweist:
    - 100 Gewichtsteile mindestens eines Kautschuks, ausgewählt unter Naturkautschuk, synthetischem Polyisoprenkautschuk, Styrol-Butadien-Kautschuk und Polybutadienkautschuk;
    - 20 bis 150 Gewichtsteile eines Verstärkerfüllstoffs; und
    - 0,05 bis 20 Gewichtsteile einer Verbindung, die unter Isophthalsäuredihydrazid und 2-Hydroxy-3-naphthoesäurehydrazid ausgewählt ist.
- 45 2. Verwendung eine Kautschukzusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß die Verbindung 2-Hydroxyl-3-naphthoesäurehydrazid ist.
  - 3. Verwendung einer Kautschukzusammensetzung nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß der Kautschuk Naturkautschuk oder synthetischer Polyisoprenkautschuk ist.
  - Verwendung einer Kautschukzusammensetzung nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß die Verbindung in einem Anteil von 0,1 bis 5 Gewichtsteilen vorhanden ist.
- Verwendung einer Kautschukzusammensetzung nach Anspruch 4, dadurch gekennzeichnet, daß die Verbindung 55 in einem Anteil von 0,25 bis 5 Gewichtsteilen vorhanden ist.
  - 6. Verwendung einer Kautschukzusammensetzung nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß der Verstärkerfüllstoff Ruß ist.

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# Revendications

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- 1. Utilisation d'une composition de caoutchouc ayant des propriétés améliorées de faible génération de chaleur dans un pneumatique, comprenant:
  - 100 parties en poids d'au moins un caoutchouc choisi parmi un caoutchouc naturel, un caoutchouc de polyisopréne synthétique, un caoutchouc styrène-butadiène et un caoutchouc de polybutadiène;
  - 20 à 150 parties en poids d'une charge renforçante; et
  - 0,05 à 20 parties en poids d'un composé choisi parmi le dihydrazide isophtalique et l'hydrazide 2-hydroxy-3-naphtoïque.
- 2. Utilisation d'une composition de caoutchouc selon la revendication 1, caractérisée en ce que ledit composé est l'hydrazide 2-hydroxy-3-naphtoïque.
- 15 3. Utilisation d'une composition de caoutchouc selon la revendication 1 ou 2, caractérisée en ce que ledit caoutchouc est un caoutchouc naturel ou un caoutchouc de polyisoprène synthétique.
  - **4.** Utilisation d'une composition de caoutchouc selon l'une quelconque des revendications 1 à 3, caractérisée en ce que ledit composé est présent en une proportion de 0,1 à 5 parties en poids.
  - **5.** Utilisation d'une composition de caoutchouc selon la revendication 4, caractérisée en ce que ledit composé est présent en une proportion de 0,25 à 5 parties en poids.
- **6.** Utilisation d'une composition de caoutchouc selon l'une quelconque des revendications 1 à 5, caractérisée en ce que ladite charge renforçante est le noir de carbone.

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